



Announcements

Cheat Sheet Vote

People who don't show up to discussion sections on Friday may be dropped from the course to make room for others. If you have a valid excuse for missing discussion write me.

New Office Hours for Me:

Monday 10-11:15am or by appointment.



Phase Changes and Chemical Reactions

Topics for today's discussion:

- 1) A thought problem
- 2) Review of Path Dependent and Path Independent Variables.
- 3) Thermodynamics of Phase Changes
- 4) Enthalpies of Chemical Reactions
- 5) Bond Energy and Enthalpy
- 6) Molecular Interpretation of Energy and Enthalpy



Concept Question

The air pressure in your bike tire registers as 15 psi on a pressure gauge (That is, it is 1 atm *above* the outside pressure).

A) First, you use a hand pump to increase the gauge pressure from 15-30 psi.

B) Then you continue to pump until the gauge reads 45 psi.

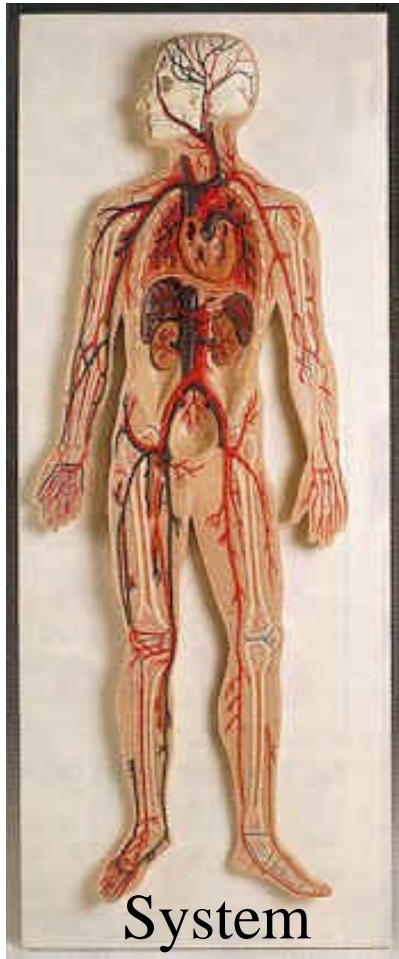
Compare the amount of work you had to do in steps A and B

1. $|W_A| > |W_B|$

2. $|W_A| = |W_B|$

3. $|W_A| < |W_B|$

Concept of Complex Conversions



How do we analyze the thermodynamics of complex systems?

How do we follow energy transformation?

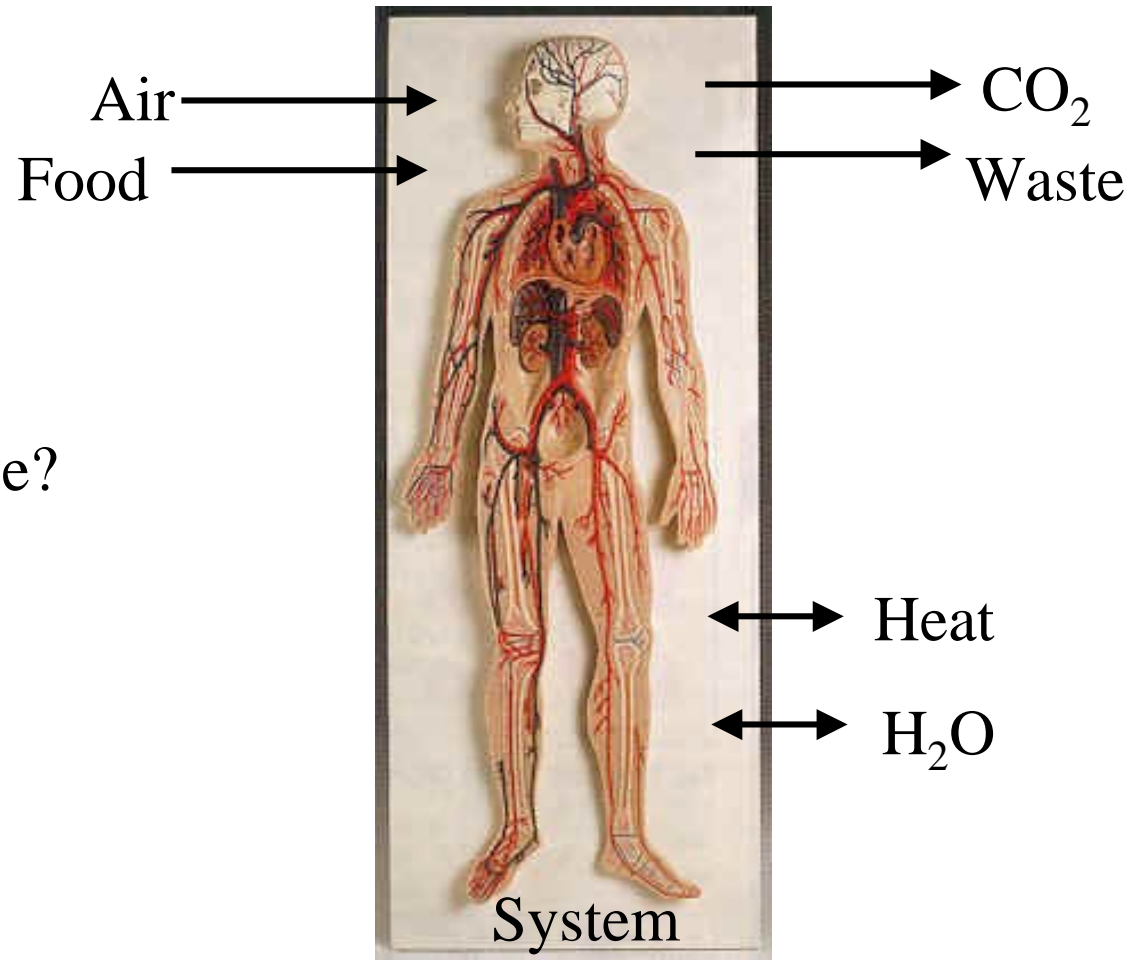
First we must define system and surroundings:

What kind of system is this?

What are the constraints on the system?

Surroundings

Concept of Complex Conversions



How do P,V,T,n behave?

How about q and w?

Surroundings



Thermodynamic Variables: AGAIN!

We've been talking mostly about the first law, heat and work.

We've defined the internal energy, E .

E is made up of

1) Potential Energy

a) Molecular rearrangements

c) Dissolution

b) Aggregation

d) Reactions

2) Kinetic Energy

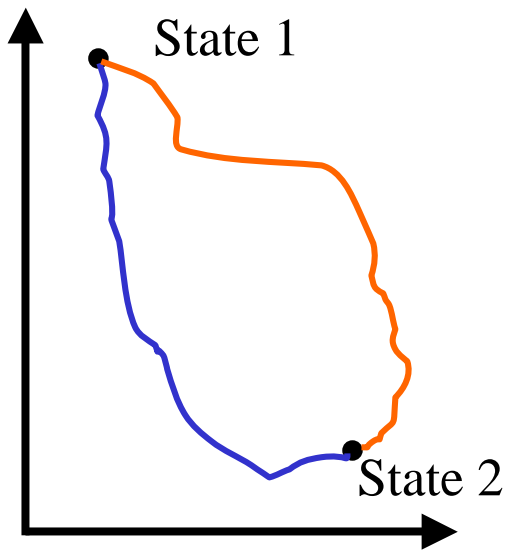
a) Molecular Vibrations

c) Translations

b) Rotations

All these properties are inherent to a particular material and can be dependent on temperature.

Energy is a Property of State: Again!



$$E = E(T, V, P, n) \longrightarrow \Delta E = E_2 - E_1$$

In integral form:

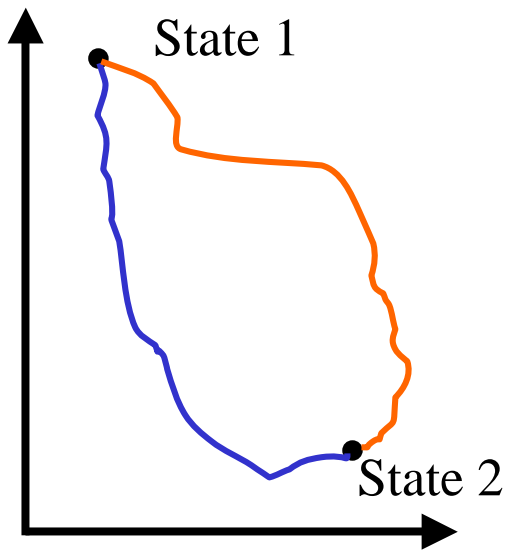
$$\Delta E = \int_1^2 dE = E_2 - E_1 \longrightarrow \oint dE = 0$$

dE is called an *exact differential* since it may be directly integrated to produce the variable.

Heat and Work are *inexact differentials*. It is not, in general possible to write down equations like that for energy.

Though for adiabatic paths: dw appears like an exact differential.
And for isochoric paths: dq appears like an exact differential.

Path Dependence and Independence



q and w are path dependent variables.

A state change that occurs over the blue path has q_{blue} , w_{blue} .

Over the red path we get q_{red} , w_{red} .

All we know from the 1st Law is:

$$\Delta E_{\text{red}} = \Delta E_{\text{blue}}$$

$$q_{\text{blue}} + w_{\text{blue}} = q_{\text{red}} + w_{\text{red}}$$

but $q_{\text{blue}} \neq q_{\text{red}}$ in general



Measuring Energy

So what is energy as a function of temperature (holding volume constant)?

$$\Delta E = q + w$$

If we consider *only* pressure volume work then at constant volume...

$$\Delta E = q$$

And since we know that $C_V = (dq/dT)_V$

$$\Delta E = \int_{T_1}^{T_2} C_V dT$$

What are the assumptions about C_V ? How do we expect it to change with T, P, V?

This is valid for solids liquids and gases, and for pure materials and for mixtures.



Measuring Enthalpy

Remember $\Delta H \equiv \Delta E + PV$

Since both ΔE and PV are state properties, ΔH must be a state property. It is therefore an *exact differential*!

Thus basic calculus applies:

$$dH = dE + d(PV) = dE + PdV + VdP$$

Since for reversible *pressure-volume* systems,

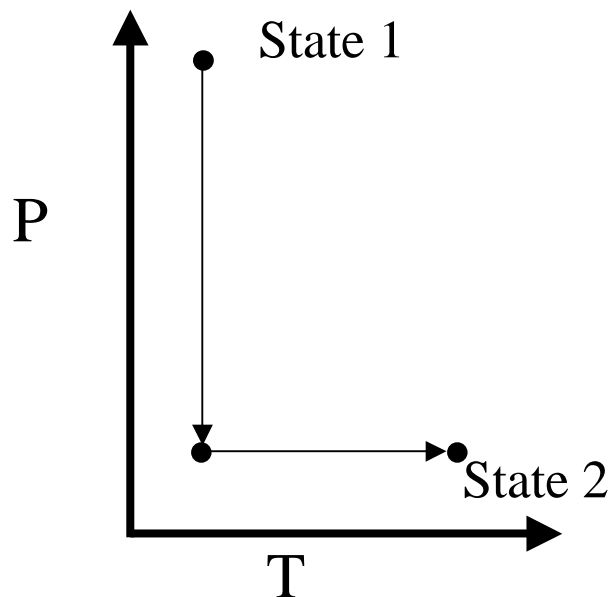
$$dE = dq + dw = dq - PdV$$

$$dH = dq - VdP$$

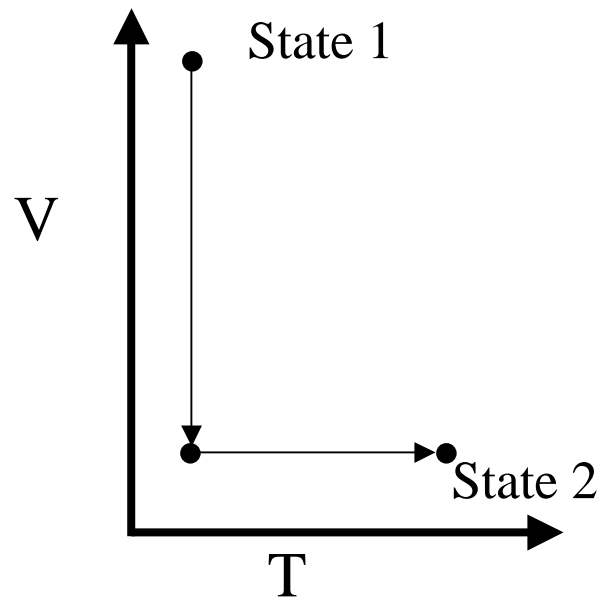
So for constant volume pressure processes:

$$\Delta H = q_p$$

Calculating ΔE and ΔH for Ideal Gases



$$\Delta E = q_T + w_T + q_P + w_P$$



$$\Delta E = q_T + w_T + q_V + w_V$$

Since for an ideal gas $PV=nRT$ and we know that the change in energy for an ideal isothermic change is zero...

$$\begin{aligned}\Delta E &= q_P + w_P = C_P(T_2 - T_1) - nR(T_2 - T_1) \\ \Delta H &= \Delta E + (P_2V_2 - P_1V_1) = \Delta E + nR(T_2 - T_1) \\ &= C_P(T_2 - T_1)\end{aligned}$$

$$\begin{aligned}\Delta E &= q_V + w_V = C_V(T_2 - T_1) + 0 \\ \Delta H &= (C_V + nR)(T_2 - T_1)\end{aligned}$$

So $C_P = C_V + nR$ for an ideal gas.

For liquids and solids:

$$C_P \approx C_V$$

Heat Capacity and Changes of State

In calculating the above we have assumed that the heat capacity is independent of temperature.

But we believe:

$$C_{\text{solid}} \neq C_{\text{liquid}} \neq C_{\text{gas}}$$

So there **must** be changes in heat capacity with temperature.

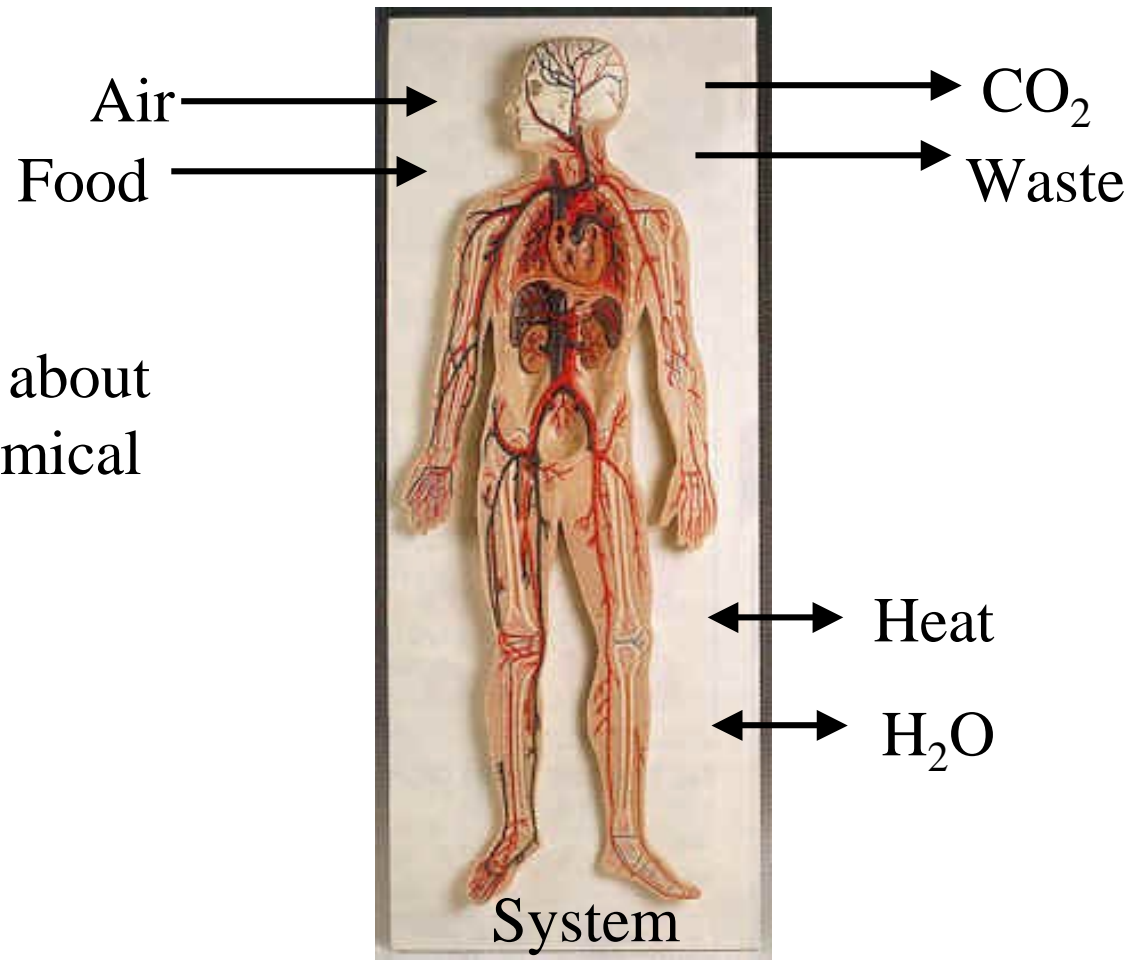
Even within a phase C can change. Often this is expressed as a power series:

$$\bar{C} = a + bT + cT^2$$

Heat capacity generally increases with temperature? (**Why?**)

Concept of Complex Conversions

So now we are talking about phase changes and chemical conversion.



Surroundings



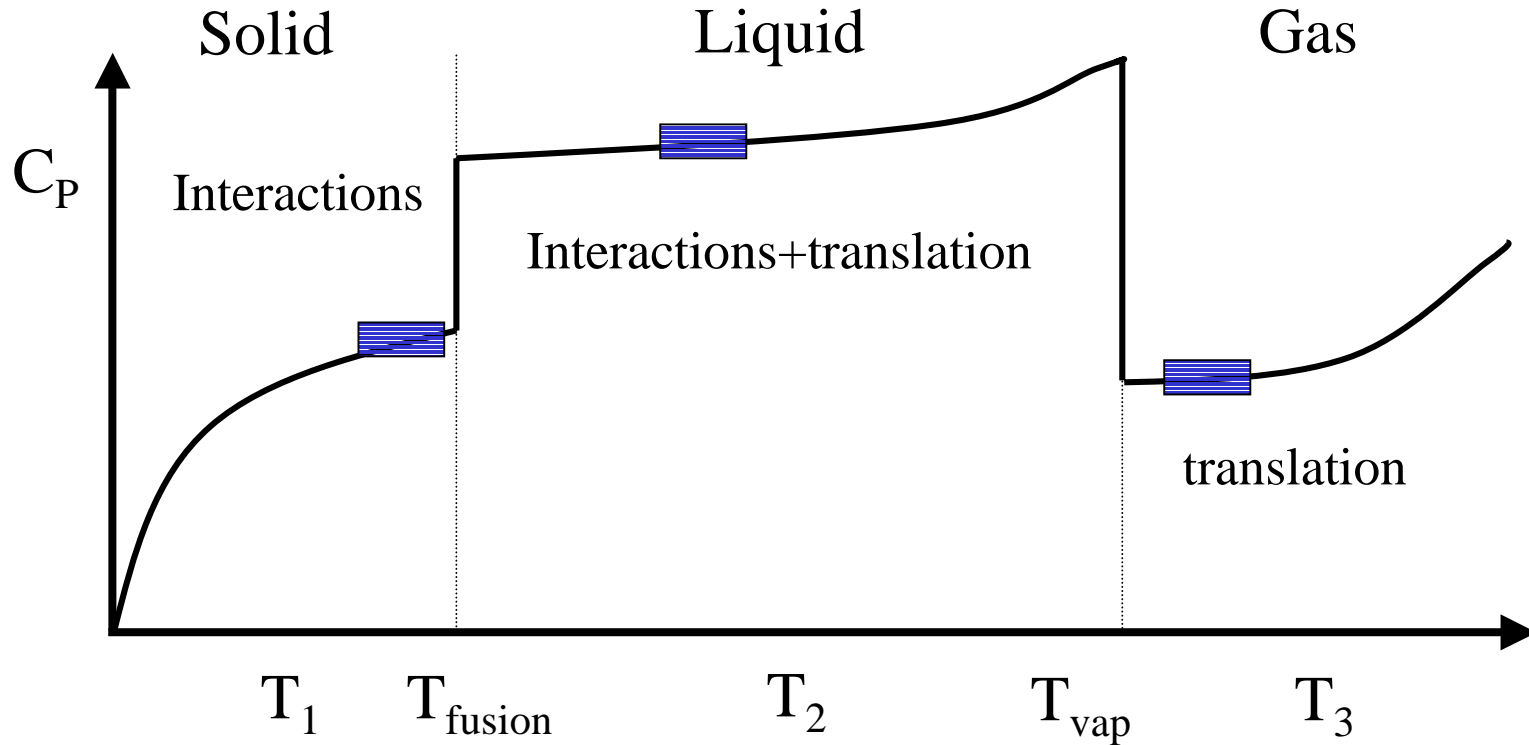
Types of Phase Changes

Physical changes

fusion (melting)	= solid	to	liquid
freezing	= liquid	to	solid
vaporization	= liquid	to	gas
condensation	= gas	to	liquid
sublimation	= solid	to	gas

Heat Capacity and Changes of State

But during a phase change, the heat capacity changes discontinuously:



$$C = C_{\text{trans}} + C_{\text{rot}} + C_{\text{vib}} + C_{\text{elec}} + \dots$$

The Energetics of Phase Transitions

So say we wish to vaporize some amount of water at a particular temperature. What do we have to do?

Well--- there are many paths to take. Let's consider primarily reversible paths, at constant pressure. (Basic lab conditions).

For a constant pressure process:

$$w_p = -P \Delta V = -P (V_{\text{phase2}} - V_{\text{phase1}})$$

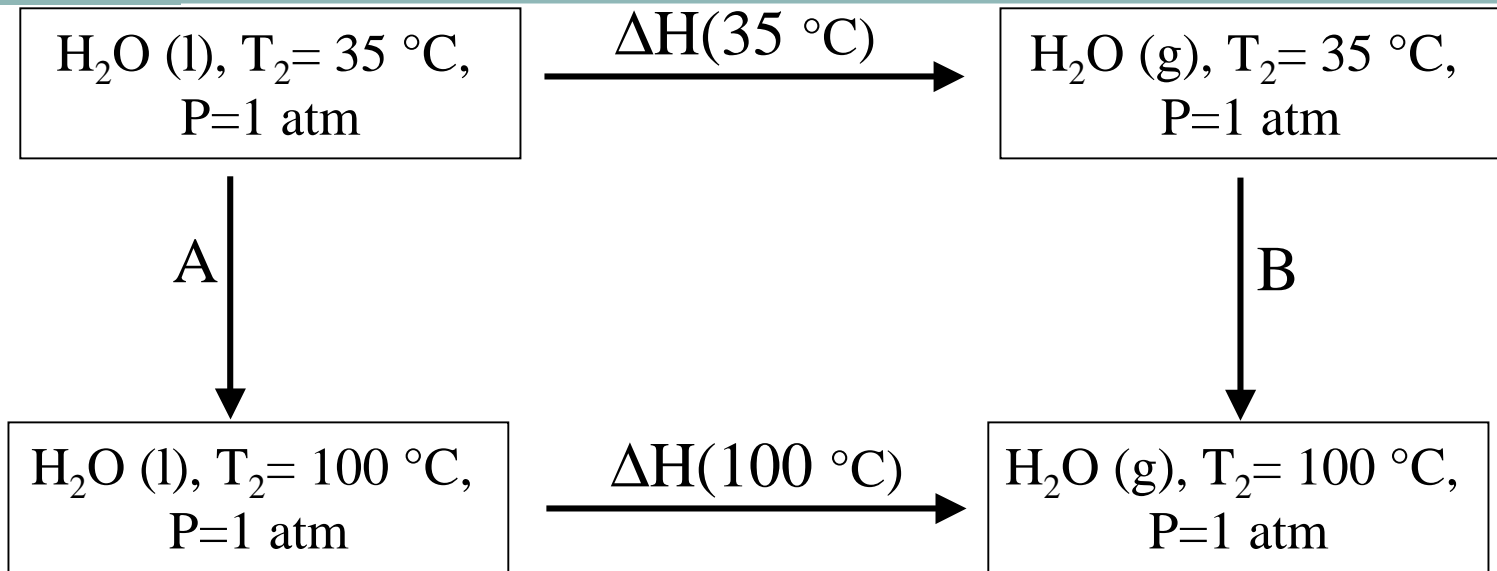
We also know

$$\Delta H = q_p$$

Since we are talking about constant P, and only allowing PV work

$$\Delta E = \Delta H - P(\Delta V)$$

The Energetics of Phase Transitions



Assuming C_P constant over this range:

$$\Delta H(35\text{ }^\circ\text{C}) = C_{P(l)} \Delta T_A + \Delta H(100\text{ }^\circ\text{C}) + C_{P(g)} \Delta T_B$$

$$\text{Since } \Delta T_A = -\Delta T_B \quad \Delta H(35\text{ }^\circ\text{C}) = \Delta H(100\text{ }^\circ\text{C}) + \Delta C_P (-65\text{ }^\circ\text{C})$$

If we calculate this from tabular value we get **2443 kJ/kg**.

The measured value is **2447 kJ/kg**. (Why?)

Phase Changes and Volume Considerations

Freezing a liquid to a solid:

$$\Delta E = \Delta H_{\text{freezing}} - P \Delta V$$

Here you simply can't ignore V of either phase. But difference between ΔE and ΔH will be small.

Vaporizing a liquid to a gas:

$$\begin{aligned}\Delta E &= \Delta H_{\text{vaporization}} + (PV)_{\text{liquid}} - (PV)_{\text{gas}} \\ &\cong \Delta H_{\text{vaporization}} - nRT\end{aligned}$$

Here the volume of liquid can be approximated as so much smaller than the volume of gas produced that it can be ignored.

ΔE and ΔH will be very different!



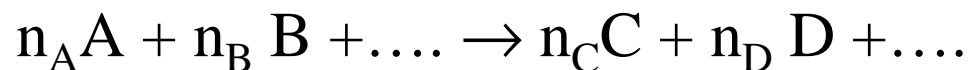
Chemical Changes

Chemical changes

Overall chemical reactions

Breaking of molecular bonds

We are now going to consider a chemical changes:



We will mostly be considering changes at constant P so that the enthalpy of the reaction is equal to the heat evolved.

Two Basic Rules of Reaction Enthalpy

We generally speak about reaction enthalpy because most chemical processes occur at constant pressure, thus, the heat generated by the reaction is a direct measure of the enthalpy.

Rule 1: The enthalpy of a particular reaction at standard temperature and pressure is given by:

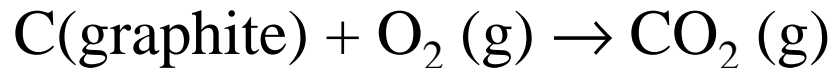
$$\Delta H = \sum_{\text{products}} H_{\text{products}} - \sum_{\text{reactants}} H_{\text{reactants}}$$

Rule 2: The enthalpy of a particular overall reaction can be derived by summing the enthalpy of a set of subreactions (**Hess's law of heat summation**)



Example: Rule 1

Rule 1:



$$\Delta H = H_{\text{CO}_2} - H_{\text{C}(\text{graphite})} - H_{\text{O}_2} = -393.51 \text{ kJ/mol}$$

Note: $H_{\text{C}(\text{graphite})} = H_{\text{O}_2} = 0$

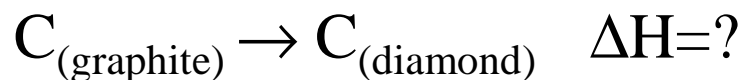
Note also that this is at Standard Temperature and Pressure:

$$\Delta H = \Delta H^\circ_{298\text{K}}$$

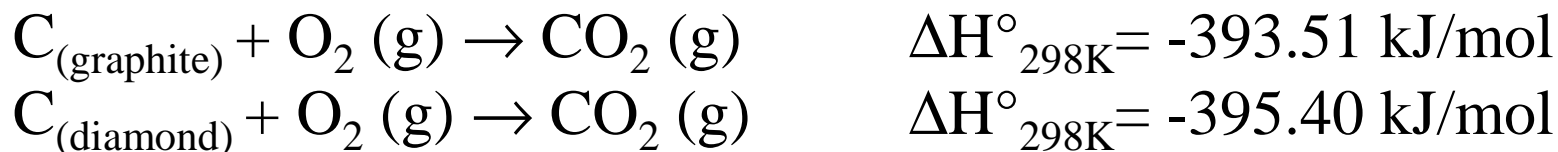
Example: Rule 2

Rule 2: Making Diamonds from Pencils

We want the enthalpy for



But we have:



Subtraction gives the correct overall reaction. So

$$\begin{aligned} \Delta H &= (\text{H}_{\text{CO}_2} - \text{H}_{\text{C}(\text{graphite})} - \text{H}_{\text{O}_2}) - (\text{H}_{\text{CO}_2} - \text{H}_{\text{C}(\text{diamond})} - \text{H}_{\text{O}_2}) \\ &= \text{H}_{\text{C}(\text{graphite})} - \text{H}_{\text{C}(\text{diamond})} \\ &= -393.51 + 395.40 = 1.89 \text{ kJ/mol} \end{aligned}$$



Vocabulary

When

$$\Delta H < 0$$

Reaction is Exothermic

$$\Delta H > 0$$

Reaction is Endothermic

$$\Delta H = 0$$

Reaction is Thermoneutral

Generally, the more exothermic the reaction the more likely a reaction will occur spontaneously... but there are other things to consider.

We will have to consider whether or not the molecules are likely to be in a configuration that allows the reactions to occur for one.



Next Time

Next time we'll go into the thermodynamics of chemical reactions (and phase changes) in more detail.

And we'll consider some general questions about biochemical processes that should be considered while doing thermodynamics:

- 1) What is the chemistry of the reactions?
- 2) What is the energy and enthalpy of the reactions?
- 3) Will this reaction occur spontaneously? (How long will it take?)
- 4) Which direction will the reaction occur?

We may even get to the second law and the concept of entropy!



Reading #2

Reading TSW:

chapter 2, pages 41-59

chapter 3, pages 67-80